

## SELF-ADHESIVE ADDITION-CROSSLINKING SILICONE COMPOSITIONS

### TECHNICAL FIELD

5 The invention relates to self-adhesive addition-crosslinking silicone compositions and addition-crosslinked silicone elastomers and composite materials prepared therefrom.

### BACKGROUND ART

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10 It is known that the adhesion of addition-crosslinked silicone elastomers to numerous substrates, such as plastics, metals and glasses, is poor, i.e. if an addition-crosslinking silicone elastomer material is applied to a substrate and then crosslinked, the silicone elastomer formed can, as a rule, be peeled away from the substrate surface without problems. Only small tensile forces; frequently, even spontaneous delamination of the silicone elastomer from the substrate is found. However, since strong and permanent adhesion of the silicone elastomer to the  
15 substrate is of primary importance in numerous applications, a large number of special measures have been proposed for achieving a strong bond between substrate and silicone elastomer.

20 In principle, the adhesive strength of the silicone elastomer/substrate composite can be increased by suitably changing the chemical and/or physical characteristics of the substrate or its surface prior to application of the addition-crosslinking silicone elastomer composition. This can be effected, for example, by pretreating the substrate surface with adhesion-promoting additives (so-called primers), by subjecting the substrate surface to a plasma treatment, by formulating the substrate to contain special additives, by selectively adjusting the morphology of the substrate,  
25 by increasing the surface roughness, etc. These measures have, inter alia, the disadvantage that additional process steps are required. As the characteristics of the substrate often have to meet special requirements, use of these methods of increasing adhesive strength is often not possible.

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The adhesive strength of the silicone elastomer/substrate composite can also be increased by selectively changing the chemical and/or physical characteristics of the addition-crosslinking silicone elastomer material. Numerous adhesion-promoting additives are known which, when mixed with the uncrosslinked silicone material, give rise to self-adhesion of the resulting silicone elastomer to various substrates. These include compounds which contain highly reactive functional groups, such as alkoxy, epoxy, carboxyl, amino, etc., these groups generally being chosen so that the adhesion promoter is capable of reacting both with the substrate and with a silicone elastomer component. Although such adhesion promoters may make it possible to dispense with a pretreatment of the substrate, the adhesive strength achieved frequently does not meet the desired requirements. In addition, an increase in the adhesive strength by means of higher content of these adhesion promoters is limited, since the highly reactive groups contained exhibit increasingly disadvantageous effects on performance characteristics such as shelf-life, crosslinking characteristics (inhibition), toxicological safety, etc. For these reasons, interest focused on keeping the content of adhesion promoters as low as possible.

EP-A-686 671 describes a self-adhesive adhesion-crosslinking material which employs no special adhesion promoter, because the adhesion-promoting component is either an organohydrogenpolysiloxane which has on average at least two SiH groups per molecule and whose monovalent Si-bonded radicals comprise at least 12 mol% of hydrocarbon radicals having an aromatic ring; or is a compound which has on average at least one SiH group per molecule and contains a group consisting of two aromatic rings, the two aromatic rings being separated from one another by  $-R^{13}R^{14}Si-$ ,  $-R^{13}R^{14}SiO-$ ,  $-OR^{13}R^{14}SiO-$  or  $-R^{13}R^{14}SiOR^{13}R^{14}Si-$ , the radicals  $R^{13}$  and  $R^{14}$  being monovalent hydrocarbon radicals. The adhesion-promoting component can thus simultaneously function as the crosslinking agent of the silicone elastomer material. Good adhesion to organic plastics (especially ABS) is achieved with this composition, while at the same time the cured or partially cured products exhibit good demoldability from the metallic vulcanization mold (chromium- or nickel-coated steel mold or mold of an aluminum alloy). The high content of greater than 12 mol% of radicals containing aromatic rings in the SiH-containing, adhesion-promoting component results, however, in considerable incompatibility with the

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- a) the SiH crosslinking agent contains at least 20 SiH groups, other radicals being aliphatically saturated,
- b) an alkoxy silane and/or alkoxy siloxane having epoxy functional groups is/are present, and
- c) a peroxide is optionally present.

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an organic plastic. However, the composition described in EP-A-875 536 has the disadvantage that sufficient adhesive strength can be achieved only with the use of

very SiH-rich crosslinking agents having on average at least 20 SiH groups per molecule. In the examples there, crosslinking agents having 30 SiH groups per molecule are used. The use of such polyfunctional crosslinking agents considerably reduces the shelf-life of addition-crosslinking silicone rubber mixtures, i.e. the flowability is considerably impaired, which may lead to stiffening of the material. As a result, proper processing of the material, for example by injection molding, is no longer possible. In addition, in order to achieve high adhesive strength, it is necessary to use relatively large amounts of alkoxysilane/alkoxysiloxane having epoxy functional groups, with the result that the crosslinking rate is considerably reduced. Although this can be partly compensated by using a peroxide, as described in EP-A-875 536, only peroxides having a low initiation temperature, such as the 2,4-dichlorobenzoyl peroxide described, are suitable for this purpose, due to the necessarily low crosslinking temperature (softening of the organic plastic). These peroxides on the one hand are toxicologically very unsafe owing to the cleavage products and secondary products liberated (PCB problem) and on the other hand further impair the shelf-life of the material.

In summary, it may be said that none of the conventional addition-crosslinking silicone elastomer compositions satisfactorily meet the requirements set for a self-adhesive silicone elastomer material which is to be used in particular for the production of composite shaped articles or for casting electric/electronic parts, namely:

- a) good flowability and shelf-life,
- b) high crosslinking rate at relatively low temperatures,
- c) high adhesive strength on organic plastics, metals and glasses,
- d) easy demoldability from vulcanization molds,
- e) toxicological safety,
- f) high level of performance characteristics, especially (transparency, noncorrosiveness, and good mechanical property profile.



5         $R^5$  is a bivalent, optionally halogen-substituted hydrocarbon radical Si-bonded at both ends, optionally containing O, N, S or P atoms and having 6 to 20 carbon atoms, and c, d, e and f denote positive numbers, with the proviso that the organohydrogenpolysiloxane (B) contains on average 3 to less than 20 SiH groups per molecule, that the relationship:  $0.05 < 100 (d+e)/(c+d+e+f) < 12$  is fulfilled, and that the viscosity of the organohydrogenpolysiloxane (B),  
10        determined at 25°C, is 1 mPa·s to 100 Pa·s.

$$\text{R}^g\text{R}^h\text{R}^i\text{SiO}_{(4-g-h-i)/2} \quad (3)$$

**R<sup>7</sup>** is a hydrogen radical, a hydroxyl radical or an optionally halogen- or cyano-substituted, saturated monovalent hydrocarbon radical optionally containing O, N, S or P atoms and having 1 to 20 carbon atoms,

**R<sup>9</sup>** is a hydrolyzable, monovalent optionally halogen-substituted hydrocarbon radical bonded to Si via an Si-O-C-, Si-O-N- or Si-N- link, optionally containing O, N, S or P atoms and having 1 to 20 carbon atoms,

(D) a hydrosilylation catalyst.

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In particular, the present composition is distinguished by the fact that

- a) the crosslinking rate is scarcely reduced,
- b) the transparency of the crosslinked silicone elastomers is not impaired,
- c) there is no need to accept any disadvantageous changes in the mechanical elastomer properties,
- d) the adhesion-promoting component (B) simultaneously acts as a crosslinking agent (no additional SiH crosslinking agent required),
- e) strong self-adhesion can be achieved even on metals without hindering the demoldability from metal vulcanization molds (it was found that the adhesion to metal shortly after crosslinking permits demolding of the silicone elastomer part; if, however, the silicone elastomer/metal

- composite is stored, the silicone elastomer grows strongly and permanently onto the metal surface within a short time),
- f) the flowability of the uncrosslinked material is scarcely impaired.

Although the adhesion-promoting component (B) of the present invention also has reduced compatibility with the other components of the material, which is evident from turbidity on mixing in, this turbidity disappears completely as soon as the material is heated for the purpose of crosslinking; this indicates a homogeneous distribution of the molecules of the crosslinking agent in the material at the time of crosslinking. If, on the other hand, the adhesion-promoting SiH-containing component (B) contains phenyl groups 12 mol% or more of the radicals, turbidity also persists at customary crosslinking temperatures and indicates inhomogeneous network formation, which can also be demonstrated on the basis of the optical properties, crosslinking characteristics, and on the basis of the mechanical properties.

The components (A), (B) and (C) may each constitute a single compound or a mixture of different compounds.

Examples of the radicals  $R^1$  are alkyl radicals such as the methyl, ethyl, propyl, isopropyl, tert-butyl, n-pentyl, isopentyl, neopentyl, tert-pentyl, n-octyl, 2-ethylhexyl, 2,2,4-trimethylpentyl, n-nonyl, and octadecyl radicals; cycloalkyl radicals such as the cyclopentyl, cyclohexyl, cycloheptyl, norbornyl, adamantylethyl and bornyl radicals; aryl or aralkyl radicals such as the phenyl, ethylphenyl, tolyl, xylyl, mesityl, and naphthyl radicals; aralkyl radicals such as the benzyl, 2-phenylpropyl and phenylethyl radicals; and those derivatives of the above radicals which are halogenated and functionalized with organic groups, such as the 3,3,3-trifluoropropyl, 3-iodopropyl, 3-isocyanatopropyl, aminopropyl, methacryloyloxymethyl, and cyanoethyl radicals. Preferred radicals  $R^1$  contain 1 to 10 carbon atoms and optionally contain halogen substituents. Particularly preferred radicals  $R^1$  are the methyl, phenyl and 3,3,3-trifluoropropyl radicals, in particular the methyl radical.



The radicals  $R^2$  are obtainable by a hydrosilylation reaction. Examples of these are alkenyl and alkynyl radicals such as the vinyl, allyl, isopropenyl, 3-butenyl, 2,4-pentadienyl, butadienyl, 5-hexenyl, undecenyl, ethynyl, propynyl and hexynyl radicals; cycloalkenyl radicals such as the cyclopentenyl, cyclohexenyl, 3-cyclohexenylethyl, 5-bicycloheptenyl, norbornenyl, 4-cyclooctenyl, and cyclooctadienyl radicals; ~~alkenyl~~ <sup>alkenyl</sup> radicals such as the styryl and styrylethyl radicals; and those derivatives of the above radicals which are halogenated and/or contain heteroatoms, such as the 2-bromovinyl, 3-bromo-1-propynyl, 1-chloro-2-methylallyl, 2-(chloromethyl)allyl, styryloxy, allyloxypropyl, 1-methoxyvinyl, cyclopentenyl, 3-cyclohexenyl, acryloyl, acryloyloxy, methacryloyl, and methacryloyloxy radicals. Preferred radicals  $R^2$  are the vinyl, allyl and 5-hexenyl radicals, in particular the vinyl radical.

In the case of the diorganopolysiloxanes (A) of the general formula (1), the viscosity determined at 25°C is preferably 100 mPa·s to 30,000 Pa·s. More preferably, the viscosity range is from 1 to 30,000 Pa·s. Depending on the type of addition-crosslinking material, different viscosity ranges may be preferred. Viscosities from 100 to 10,000 mPa·s are particularly preferred for the materials known as RTV-2 (room temperature vulcanizing) compositions, from 1 to 100 Pa·s for LSR (liquid silicone rubber) compositions, and from 2000 to 40,000 Pa·s for HTV (high temperature vulcanizing) compositions.

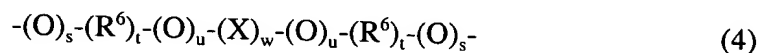
Examples of  $R^3$  are alkyl radicals such as the methyl, ethyl, propyl, isopropyl, tert-butyl, n-octyl, 2-ethylhexyl and octadecyl radicals; and cycloalkyl radicals such as the cyclopentyl, cyclohexyl, norbornyl, and bornyl radicals. Preferred radicals  $R^3$  are hydrocarbon radicals having 1 to 10 carbon atoms. A particularly preferred radical  $R^3$  is the methyl radical.

Examples of  $R^4$  (a) are the phenyl, tolyl, xylyl, biphenyl, anthryl, indenyl, phenanthryl, naphthyl, benzyl, phenylethyl and phenylpropyl radicals, and those derivatives of the above radicals which are halogenated and functionalized with organic groups, such as the o-, m- or p-chlorophenyl, pentafluorophenyl, bromotolyl, trifluorotolyl, phenoxy, benzyloxy, benzyloxyethyl, benzoyl, benzoyl-

oxy, p-tert-butylphenoxypropyl, 4-nitrophenyl, quinolinyl, and pentafluorobenzoyloxy radicals.

5 Examples of hydrocarbon radicals  $R^4$  (b) having 2 to 20 carbon atoms are the 3-chloropropyl, 3-bromopropyl, 3,3,3-trifluoropropyl, 2-fluoroethyl, 1,1-dihydroperfluorododecyl, and 2-cyanoethyl radicals. Particularly preferred radicals  $R^4$  are the phenyl radical and the 3,3,3-trifluoropropyl radical.

Preferred radicals  $R^5$  correspond to the general formula (4)



in which

10 s, t, u and w, independently of one another, denote the values 0, 1 or 2,

$R^6$  may be identical or different and denotes a bivalent, optionally halogen-substituted hydrocarbon radical which optionally contains O, N, S or P atoms, is free of aliphatically unsaturated aliphatic groups and contains 1 to 10 carbon atoms, such as  $-\text{CH}_2-$ ,  $-\text{CH}_2-\text{CH}_2-$ ,  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ ,  $-\text{CF}_2-$ ,  $-\text{CH}_2-\text{CF}_2-$ ,  $-\text{CH}_2-\text{CH}(\text{CH}_3)-$ ,  $-\text{C}(\text{CH}_3)_2-$ ,  $-\text{CH}_2-\text{C}(\text{CH}_3)_2-$ ,  $-\text{C}(\text{CH}_3)_2-\text{CH}_2-$ ,  $-\text{CH}_2-\text{CH}_2-\text{O}-$  or  $-\text{CF}_2-\text{O}-$ ,

15  $-(X)-$  denotes a bivalent radical which may be  $-\text{Ph}-$ ,  $-\text{Ph}-\text{O}-\text{Ph}-$ ,  $-\text{Ph}-\text{S}-\text{Ph}-$ ,  $-\text{Ph}-\text{SO}_2-\text{Ph}-$ ,  $-\text{Ph}-\text{C}(\text{CH}_3)_2-\text{Ph}-$ ,  $-\text{Ph}-\text{C}(\text{CF}_3)_2-\text{Ph}-$ ,  $-\text{Ph}-\text{C}(\text{O})-\text{Ph}-$ , cyclohexylene or norbornylene,  $-\text{Ph}-$  designating a phenylene group. A particularly preferred radical  
20  $R^5$  is the phenylene radical.

The organohydrogenpolysiloxane (B) preferably contains 5 to 18 SiH groups per molecule. The viscosity of the component (B), measured at 25°C, is preferably 2 mPa·s to 1 Pa·s. Owing to the labile nature of the SiH group, the component (B) may have a low content, typically <100 ppm by weight, of Si-bonded OH groups, due to the method of preparation.

Examples of hydrocarbon radicals  $R^7$  are alkyl radicals such as the methyl, ethyl, n-propyl, isopropyl, tert-butyl, n-pentyl, isopentyl, neopentyl, tert-pentyl,

n-octyl, 2-ethylhexyl, 2,2,4-trimethylpentyl, n-nonyl and octadecyl radicals; cycloalkyl radicals such as the cyclopentyl, cyclohexyl, cycloheptyl, norbornyl, adamantylethyl, and bornyl radicals; aryl radicals such as the phenyl, ethylphenyl, tolyl, xylyl, mesityl, and naphthyl radicals; aralkyl radicals such as the benzyl, phenylethyl, and phenylpropyl radicals; alkenyl or alkynyl radicals such as the vinyl, allyl, isopropenyl, 3-butenyl, 2,4-pentadienyl, butadienyl, 5-hexenyl, undecenyl, ethynyl, propynyl and hexynyl radicals; cycloalkenyl radicals such as the cyclopentenyl, cyclohexenyl, 3-cyclohexenylethyl, 5-bicycloheptenyl, norbornenyl, 4-cyclooctenyl, and cyclooctadienyl radicals; aralkenyl radicals such as the phenylethenyl and phenylethynyl radical; and those derivatives of the above radicals which are halogen-substituted or contain heteroatoms, such as the 3-chloropropyl, 3-bromopropyl, decafluoro-1,1,2,2-tetrahydrooctyl, (p-chloromethyl)phenyl, (p-chloromethyl)phenethyl, hydroxymethyl, hydroxyethyl, hydroxypropyl, hydroxybutyl, 2-bromovinyl, 2-allyloxymethyl, acetyl, acetoxymethyl, acetoxylethyl, acetoxypentyl, 3-phenoxypropyl, benzoyloxypentyl, mercaptopentyl, cyanoethyl, cyanopentyl, 3-cyanobutyl, 3-isocyanatopentyl, 2-(carbomethoxy)ethyl, 10-(carbomethoxy)decyl, 2-(carboxymethylthio)ethyl, 3-carboxypentyl, aminomethyl, aminoethyl, aminopentyl, aminoethyl, aminoethylaminopentyl, 3-(N-allylamino)pentyl, (aminoethylaminomethyl)phenethyl, m-aminophenyl, 3-(m-aminophenoxy)pentyl, 3-acryloyloxypentyl, 3-acryloyloxy-2-hydroxypentyl, 4-(acryloyloxymethyl)phenethyl, methacryloyloxymethyl, methacryloyloxyethyl, and methacryloyloxypentyl radicals. Preferred radicals  $R^7$  are the methyl, ethyl, propyl, butyl, octyl, vinyl, allyl, phenyl, 3,3,3-trifluoropentyl and cyanopentyl radicals. Particularly preferred radicals  $R^7$  are the methyl, vinyl and phenyl radicals.

Examples of the radicals  $R^8$  are the epoxyethyl, 2,3-epoxypropyl, 3,4-epoxybutyl, 5,6-epoxyhexyl, 9,10-epoxydecyl, glycidyloxy, 3-glycidyloxypentyl, glycidyloxyisobutyl, 2-methylglycidyloxypentyl, 3-phenylglycidyloxypentyl, glycidyloxyphenylnonyl, glycidyloxybenzylethyl, 3,4-epoxycyclohexyl, 2-(3,4-epoxycyclohexyl)ethyl, 3-(3,4-epoxycyclohexyl)propyl, 1,4-epoxycyclohexyl, and 2-(1,4-epoxycyclohexyl)ethyl radicals. Preferred radicals  $R^8$  are the 3,4-epoxycyclohexyl, 3-(3,4-epoxycyclohexyl)propyl and glycidyloxypentyl radicals.  $R^8$

preferably has 2 to 10 carbon atoms. A particularly preferred radical  $R^8$  is the glycidyloxypropyl radical.

$R^9$  denotes a hydrolyzable, monovalent, optionally halogen-substituted hydrocarbon radical bonded to Si via an Si-O-C-, Si-O-N- or Si-N-link, optionally containing O, N, S or P atoms and having 1 to 20 carbon atoms.

Examples of the radicals  $R^9$  are

- a) alkoxy, alkenoxy or aryloxy groups of the general formula  $-OR^{10}$ , such as the methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, tert-butoxy, 2-ethylbutoxy, 2-ethylhexyloxy, vinyloxy, allyloxy, isopropenyloxy, cyclobutenyloxy, cyclohexenyloxy, 1,3-butadienyloxy, propargyloxy, phenoxy, benzyloxy, and m- and p-vinylbenzyloxy radicals;
- b) acyloxy groups of the general formula  $-OCOR^{10}$ , such as the formyloxy, acetoxy, 2-ethylhexanoyloxy, acryloyloxy, methacryloyloxy, benzoyloxy, and norbornyl-acetoxy radicals;
- c) amino groups of the general formula  $-NH_2$ ,  $-NHR^{10}$ , and  $-NHR^{10}_2$ , such as the dimethylamino, diisopropylamino, allylamino, n-butylamino, sec-butylamino, and cyclohexylamino radical;
- d) oxime groups of the general formula  $-ON=CH_2$ ,  $-ON=CHR^{10}$ , and  $-ON=CR^{10}_2$ , such as the methyl ethyl ketoxime, methyl isobutyl ketoxime, methyl n-amyl ketoxime, and dimethyl ketoxime radicals;
- e) amido groups of the general formula  $-NH-C(=O)-R^{10}$  or  $-NR^{10}-C(=O)-R^{10}$ , such as the N-methylbenzamido and N-methylacetamido radicals;
- f) aminoxy groups of the general formula  $-ONH_2$ ,  $-ONHR^{10}$  or  $-ONR^{10}_2$ , such as the hydroxylamino radical; and
- g) those derivatives of the abovementioned radicals which are halogen-substituted or contain heteroatoms or have an otherwise complex composition, such as p-aminophenoxy, 2-methoxyethoxy, 1-methoxy-2-propoxy, 1-methoxy-isopropenyloxy, methoxyethoxyethoxy, 1-methoxy-2-methylpropenyloxy, acryloyloxymethoxy, methacryloyloxy(polyethyleneoxy), furyloxy, and N-vinyl-formamido radicals, and  $-O-Ph-C(=O)-Ph$ ,  $-O-C(CF_3)=CH-C(=O)-CF_3$ ,  $-O-C(CH_3)=CH-C(=O)-CH_3$ ,  $-O-C(CH_3)_2-CH=CH_2$ ,  $-NH-C(=O)-CH_3$ ,

-O-C(=O)-CH<sub>2</sub>Br, -O-C(=O)-CF<sub>3</sub>, -O-C(=O)-C≡CH or -O-CH<sub>2</sub>-C(=O)-O-Si(CH<sub>3</sub>)<sub>3</sub>,

5 where the radicals R<sup>10</sup> represent monovalent aliphatic or aromatic, saturated or unsaturated, optionally halogen-substituted hydrocarbon radicals having 1 to 10 carbon atoms. Preferred radicals R<sup>9</sup> are the alkoxy radicals such as the methoxy, ethoxy, propoxy, and butoxy radicals. The particularly preferred radical R<sup>9</sup> is the methoxy radical. A particularly suitable organosilicon compound (C) is glycidyloxypropyltrimethoxysilane (Glymo).

10 The radicals R<sup>1</sup> to R<sup>10</sup> in all above formulae may be identical or different. Preferred heteroatoms are N, O and S. Preferred halogen substituents are F, Cl and Br.

15 Preferably 0.1 to 50 parts by weight, in particular 0.5 to 10 parts by weight, of organohydrogenpolysiloxane (B) and 0.1 to 10 parts by weight, in particular 0.5 to 5 parts by weight, of organosilicon compound (C) are used per 100 parts by weight of diorganopolysiloxane (A).

20 Hydrosilylation catalyst (D) serves as a catalyst for the hydrosilylation addition reaction between the aliphatically unsaturated hydrocarbon radicals R<sup>2</sup> of the diorganopolysiloxanes (A) and the silicon-bonded hydrogen atoms of the organohydrogenpolysiloxanes (B). Numerous suitable hydrosilylation catalysts are described in the literature. In principle, all hydrosilylation catalysts corresponding to the prior art and used in addition-crosslinking silicone rubber materials can be used.

25 Metals and their compounds, such as platinum, rhodium, palladium, ruthenium and iridium, preferably platinum, can be used as hydrosilylation catalysts (D). The metals can optionally be fixed on finely divided support materials, such as active carbon, metal oxides, such as alumina, or silica.

Platinum and platinum compounds are preferably used. Particularly preferred platinum compounds are those which are soluble in polyorganosiloxanes.

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5 The soluble platinum compounds used may be, for example, the platinum-olefin complexes of the formulae  $(\text{PtCl}_2 \cdot \text{olefin})_2$  and  $\text{H}(\text{PtCl}_3 \cdot \text{olefin})$ , alkenes having 2 to 8 carbon atoms such as ethylene, propylene, isomers of butene and of octene, and ~~cycloalkanes~~ <sup>cycloalkenes</sup> having 5 to 7 carbon atoms such as cyclopentene, cyclohexene and cycloheptene preferably being used. Further soluble platinum catalysts are the platinum-cyclopropane complexes of the formula  $(\text{PtCl}_2\text{C}_3\text{H}_6)_2$ , the reaction products of hexachloroplatinic acid with alcohols, ethers and aldehydes and mixtures thereof or the reaction product of hexachloroplatinic acid with methylvinylcyclotetrasiloxane in the presence of sodium bicarbonate in ethanolic solution. Platinum catalysts with 10 phosphorous, sulfur and amine ligands may also be used, e.g.  $(\text{Ph}_3\text{P})_2\text{PtCl}_2$ . Complexes of platinum with vinylsiloxanes, such as sym-divinyltetramethyldisiloxane, are particularly preferred.

15 The amount of hydrosilylation catalyst (D) used depends on the desired crosslinking rate and economic points of view. Preferably,  $1 \times 10^{-5}$  to  $5 \times 10^{-2}$  part by weight, in particular  $1 \times 10^{-3}$  to  $1 \times 10^{-2}$  part by weight of platinum catalysts, calculated as platinum metal, is used per 100 parts by weight of diorganopolysiloxanes (A).

20 The self-adhesive addition-crosslinking silicone compositions can optionally contain conventional further components (E), such as fillers, inhibitors, stabilizers, pigments and catalysts.

25 In order to achieve a sufficiently high mechanical strength of the crosslinked silicone rubber, it is preferable to incorporate actively reinforcing fillers as component (F) into the addition-crosslinking silicone compositions. The actively reinforcing fillers (F) preferably used are, in particular, precipitated and pyrogenic silicas, and mixtures thereof. The specific surface area of these actively reinforcing fillers should be at least  $50 \text{ m}^2/\text{g}$  or preferably in the range from 100 to  $400 \text{ m}^2/\text{g}$  according to the determination by the BET method. Such actively reinforcing fillers are very well known materials in the area of silicone rubbers.

5 The compounding of the self-adhesive addition-crosslinking silicone compositions is effected by mixing the abovementioned ingredients in any desired sequence. The crosslinking of the self-adhesive addition-crosslinking silicone compositions is preferably effected by heating, preferably at 30°C to 250°C, preferably at at least 50°C, in particular at at least 100°C, and preferably at not more than 200°C, more preferably at not more than 180°C.

The invention also relates to the addition-crosslinked silicone elastomers prepared from the crosslinkable compositions.

10 The silicone compositions can be bonded to a substrate by applying the silicone compositions to the substrate and then crosslinking them, preferably by heating to 30 to 250°C, to give a composite material. The self-adhesive addition-crosslinking silicone composition can advantageously be used in particular where good adhesive strength between the addition-crosslinked silicone elastomer and a substrate, preferably an organic polymer, metal or glass substrate, is desired. The  
15 substrate may be present as a shaped article, film or coating. The self-adhesive addition-crosslinking silicone compositions are suitable for the production of composite materials by coating, adhesive bonding or casting, and for the production of shaped articles.

20 The self-adhesive addition-crosslinking silicone compositions are particularly suitable for casting and for adhesively bonding electrical and electronic parts and for the production of composite shaped articles. Composite shaped articles are understood here as meaning a uniform shaped article comprising a composite material which is composed of a silicone elastomer part produced from the silicone compositions and at least one substrate, so that there is a strong, permanent bond  
25 between the two parts. Such a composite shaped article is preferably produced by processing an organic polymer or polymer precursor to give a shaped article, followed by bringing the silicone composition into contact with this shaped article and crosslinking. This can be effected, for example, by injection molding, by means of extrusion, and by the so-called press-molding method. Composite materials and  
30 in particular composite shaped articles can be used in a very wide range of

applications, for example in the electronics, household appliance, consumables, construction, and automotive industries, in medical technology, in the production of sport and leisure articles, etc.

In the following examples, unless stated otherwise in each case, all  
5 pressures are 0.10 MPa (abs.), and all temperatures are 20°C.

Examples:

### Substrates

The adhesion of the addition-crosslinked silicone elastomers according to the invention and comparative elastomers not according to the invention was tested on the following substrates:

- 15 a) polybutylene terephthalate (PBT): Ultradur® B4300G6 (BASF AG; 30 % GF)  
b) polyamide 6: Durethan® BKV30 (Bayer AG; 30 % GF)  
c) polycarbonate (PC): Lexan® (General Electric)  
d) aluminum (industrial quality; not primed)  
e) steel: VA stainless steel (industrial quality).

### Characterization of adhesion

(Examples 1, 2, and 3 and Comparative Examples C1 and C2

To characterize adhesive strength, 100.0 g of an addition-crosslinking liquid silicone elastomer material which is free of crosslinking agent, and contains 71.6% by weight of diorganopolysiloxane having a viscosity of 20,000 mPa·s and 28.4% by weight of a reinforcing filler and is available from Wacker-Chemie GmbH under the name ELASTOSIL® LR 3003/40 A, are thoroughly mixed with a specified amount of the adhesion-promoting additive which is prepared according to the following examples and which simultaneously serves as a crosslinking agent, and then degassed in vacuo at room temperature. This material is then immediately applied as an about 1.2 mm thick layer, by means of a doctor blade, to the respective substrate surface which has been cleaned beforehand with ethanol. A primed, hollow



**Example 1**

5.0 kg of a methylhydrogenpolysiloxane,  $\text{Me}_3\text{Si}-(\text{-O-SiH(Me)})_n\text{-O-SiMe}_3$ , which has terminal trimethylsilyloxy groups and, according to  $^{29}\text{Si}$ -NMR, has a number average chain length of  $n=53$ , and 5.0 kg of a siloxane copolymer having terminal trimethylsilyloxy groups and consisting of dimethylsilyloxy and methylphenylsilyloxy units in a molar ratio of 15.2:21.8 and having a viscosity, measured at  $25^\circ\text{C}$ , of 100 mPa·s, are initially introduced into a stirrer. 1.8 g of phosphonitrilic chloride, prepared according to US-A-4,203,913, are added at room temperature with continuous stirring. After application of a vacuum of  $<20$  mbar, stirring is carried out for 5 min and the vacuum is then broken with  $\text{N}_2$ . Stirring is then carried out for 2 h at a temperature of  $100^\circ\text{C}$ . 14 g of hexamethyldisilazane are then added and stirring is carried out for a further 15 min. Finally, a vacuum of  $<10$

5.0 kg of a methylhydrogenpolysiloxane,  $\text{Me}_3\text{Si}-(\text{-O-SiH(Me)})_n\text{-O-SiMe}_3$ , which has terminal trimethylsilyloxy groups and, according to  $^{29}\text{Si}$ -NMR, has a number average chain length of  $n=53$ , and 5.0 kg of a siloxane copolymer having terminal trimethylsilyloxy groups and consisting of dimethylsilyloxy and methylphenylsilyloxy units in a molar ratio of 15.2:21.8 and having a viscosity, measured at  $25^\circ\text{C}$ , of 100 mPa·s, are initially introduced into a stirrer. 1.8 g of phosphonitrilic chloride, prepared according to US-A-4,203,913, are added at room temperature with continuous stirring. After application of a vacuum of  $<20$  mbar, stirring is carried out for 5 min and the vacuum is then broken with  $\text{N}_2$ . Stirring is then carried out for 2 h at a temperature of  $100^\circ\text{C}$ . 14 g of hexamethyldisilazane are then added and stirring is carried out for a further 15 min. Finally, a vacuum of  $<10$

mbar is applied, the mixture is freed from volatile components with continuous stirring for 1 h at 100°C, the vacuum is broken with N<sub>2</sub>, cooling to room temperature is effected, and the reaction product is filtered. A polyorganosiloxane which has terminal trimethylsilyloxy groups, is composed of -O-Si(Me)<sub>2</sub>-, -O-SiH(Me)- and -O-Si(Me)Ph- units in a molar ratio of 15.2:63.0:21.8 and has a viscosity of 32.1 mm<sup>2</sup>/s at 25°C is obtained. The product contains on average 17 Si-H groups per molecule.

The preparation of the adhesion-promoting additive, which is used in an amount of 1.3 g per 100 g of silicone elastomer material to be crosslinked, is effected by mixing 10 parts by weight of glycidyloxypropyltrimethoxysilane with 16 parts by weight of the reaction product described above. The results of the adhesion measurements are shown in Table 1.

#### Comparative Example C1

Instead of the phenyl-containing crosslinking agent described in Example 1, a polyorganosiloxane which has terminal trimethylsilyloxy groups, contains only -O-Si(Me)<sub>2</sub>- and -O-SiH(Me)- units in a molar ratio of 29:71 and has a viscosity of 30 mm<sup>2</sup>/s at 25°C is used; this crosslinking agent contains on average 33 Si-H groups per molecule. The preparation of the adhesion-promoting additive, which is used in an amount of 1.05 g per 100 g of silicone elastomer material to be crosslinked, is effected by mixing 10 parts by weight of glycidyloxypropyltrimethoxysilane with 11 parts by weight of the phenyl-free crosslinking agent described above. This mixing ratio and the amount of adhesion-promoting additive used ensure that the addition-crosslinking silicone elastomer materials prepared according to Example 1 and Example 2 have the same content of Si-bonded hydrogen. The results of the adhesion measurements are shown in Table 1.

#### Example 2

0.05 g of phosphonitrilic chloride, prepared according to US-A-4,203,913, is added at room temperature with continuous stirring, to 150 g of a methylhydrogen-polysiloxane, Me<sub>3</sub>Si-(-O-SiH(Me))<sub>n</sub>-O-SiMe<sub>3</sub>, which has terminal trimethylsilyloxy groups and, according to <sup>29</sup>Si-NMR, has a number average chain length of n=53, and 150 g of a siloxane copolymer having terminal trimethylsiloxy groups, consisting

of dimethylsilyloxy and diphenylsilyloxy units, having a phenyl content of 19.2% by weight and having a viscosity of 85 mPa·s, measured at 25°C. After application of a vacuum of <20 mbar, stirring is carried out for 5 min and the vacuum is then broken with N<sub>2</sub>. Stirring is then carried out for 2 h at a temperature of 100°C. 0.5 g of hexamethyldisilazane is added and stirring is carried out for a further 15 min. Finally, a vacuum of <10 mbar is applied, the mixture is freed from volatile components with continuous stirring for 1 h at 100°C, the vacuum is broken with N<sub>2</sub>, cooling to room temperature is effected and the reaction product is filtered. A polyorganosiloxane which has terminal trimethylsilyloxy groups, is composed of -O-Si(Me)<sub>2</sub>-, -O-SiH(Me)- and -O-SiPh<sub>2</sub>- units in a molar ratio of 26.5:70.0:3.5 and has a viscosity of 455 mm<sup>2</sup>/s at 25°C is obtained.

The preparation of the adhesion-promoting additive, which is used in an amount of 1.3 g per 100 g of silicone elastomer material to be crosslinked, is effected by mixing 10 parts by weight of glycidyoxypropyltrimethoxysilane with 16 parts by weight of the reaction product described above.

The results of the adhesion measurements are shown in Table 1.

### Example 3

150 g of a methylhydrogenpolysiloxane, Me<sub>3</sub>Si-(-O-SiH(Me))<sub>n</sub>-O-SiMe<sub>3</sub>, which has terminal trimethylsilyloxy groups and, according to <sup>29</sup>Si-NMR, has a number average chain length of n=53, 26 g of a polydimethylsiloxane which has terminal trimethylsilyloxy groups and has a viscosity of 100 mPa·s at 25°C, and 112 g of 1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)cyclotrisiloxane are initially introduced at room temperature and mixed, with continuous stirring, with 0.05 g of phosphonitrilic chloride, prepared by US-A-4,203,913. After application of a vacuum of <20 mbar, stirring is carried out for 5 min and the vacuum is then broken with N<sub>2</sub>. Stirring is then carried out for 2 h at a temperature of 100°C. In order to deactivate the catalyst (phosphonitrilic chloride), gaseous ammonia is passed in for 15 min. Thereafter, a vacuum of <10 mbar is applied, the mixture is freed from volatile components with continuous stirring for 1 h at 100°C, the vacuum is broken with N<sub>2</sub>, cooling to room temperature is effected, and the reaction product is filtered. A polyorganosiloxane which has terminal trimethylsilyloxy groups,

composed of  $-O-Si(Me)_2-$ ,  $-O-SiH(Me)-$  and  $-O-Si(Me)(CH_2CH_2CF_3)-$  units in a molar ratio of 10.1:69.9:20.0 and which has a viscosity of  $52.3 \text{ mm}^2/\text{s}$  at  $25^\circ\text{C}$  is obtained.

5 The preparation of the adhesion-promoting additive, which is used in an amount of 1.3 g per 100 g of silicone elastomer material to be crosslinked, is effected by mixing 10 parts by weight of glycidyloxypropyltrimethoxysilane with 16 parts by weight of the reaction product described above. The results of the adhesion measurements are shown in Table 1.

### Comparative Example C2

10 The composition corresponds to the silicone elastomer material described in Example 1, except that no glycidyloxypropyltrimethoxysilane was added. The results of the adhesion measurements are shown in Table 1.

Table 1: (breaking tension in  $[N/mm^2]$ ; proportion of cohesive failure in [%])

15

Ex.	PBT		Polyamide 6		PC		Aluminum		Steel	
	$[N/mm^2]$	[%]	$[N/mm^2]$	[%]	$[N/mm^2]$	[%]	$[N/mm^2]$	[%]	$[N/mm^2]$	[%]
1	2.72	100	3.05	50	2.38	0	2.89	100	2.65	100
C1	1.60	0	1.41	0	1.51	0	1.90	0	1.98	0
2	2.56	100	3.12	30	2.33	0	3.23	100	2.55	90
3	2.22	80	2.78	40	2.08	30	2.78	100	2.25	90
C2	1.20	10	1.53	20	1.87	0	2.20	20	2.13	20

20 The values shown in Table 1 demonstrate the high adhesive strength between the addition-crosslinked silicone elastomer according to the invention (Examples 1, 2, and 3) and various organic plastics and metals. As is evident from Comparative Example C1, high adhesive strength is not achieved by the presence of component (C) alone (e.g. glycidyloxypropyltrimethoxysilane) but only in conjunction with  
25 component (B) according to the invention. As is evident from Comparative Example C2, a high adhesive strength is not achieved by the presence of the component (B)

alone but only in conjunction with component (C) according to the invention. This is evidence of a synergistic effect of the adhesion-promoting components (B) and (C) of the silicone elastomer material according to the invention.

5      **Characterization of the adhesion**  
         (Examples 4, 5, 6 and Comparative Examples C3 and C4

                 A substrate strip having dimensions  $60 \times 20 \times 2$  mm is introduced into a stainless steel compression mold and the mold is filled with the addition-crosslinking silicone elastomer material to be tested. A press cure is carried out for 5 min at a temperature of  $170^{\circ}\text{C}$  and a pressure of 30 tonnes. After removal of the laminate, the  
10      rigid substrate element is firmly clamped and the maximum parting force required to detach the adhering silicone elastomer strip in a peel test is determined. The parting force is determined according to DIN 53531 and is stated in N/mm. Ten laminates are measured per example, the parting force is determined as a mean value, and the proportion of cohesive failure is determined as a percentage. Cohesive failure of 0%  
15      means that the silicone elastomer was detached completely and without residue from the substrate surface. Cohesive failure of 100% means that the delamination took place exclusively by crack growth within the silicone elastomer.

**Example 4**

                 The composition corresponds to the addition-crosslinking silicone elastomer material  
20      according to the invention described in Example 1. The results of the measurements of the parting force are shown in Table 2.

**Example C3**

                 The composition corresponds to the addition-crosslinking silicone elastomer material, not according to the invention, described in Comparative Example C1. The results  
25      of the measurements of the parting force are shown in Table 2.

### Example 5

The composition corresponds to the addition-crosslinking silicone elastomer material according to the invention described in Example 2. The results of the measurements of the parting force are shown in Table 2.

### 5 Example 6

The composition corresponds to the addition-crosslinking silicone elastomer material according to the invention, described in Example 3. The results of the measurements of the parting force are shown in Table 2.

### Comparative Example C4

- 10 The composition corresponds to the addition-crosslinking silicone elastomer material not according to the invention, described in Comparative Example C2. The results of the measurements of the parting force are shown in Table 2.

Table 2: (parting force in [N/mm]; proportion of cohesive failure in [%])

Ex.	PBT		Polyamide 6		Aluminum		Steel	
	[N/mm]	[%]	[N/mm]	[%]	[N/mm]	[%]	[N/mm]	[%]
4	14.8	100	9.3	30	14.6	100	16.4	100
C3	7.1	20	4.9	0	7.2	10	12.8	80
5	12.3	100	11.0	30	13.3	100	15.5	100
6	11.8	80	7.7	40	10.0	90	14.4	100
C4	6.2	0	4.4	0	8.9	30	10.5	40

- 15
- 20 The values shown in Table 2 demonstrate the high adhesive strength of laminates consisting of the addition-crosslinked silicone elastomer according to the invention (Examples 4, 5 and 6) and organic plastics and metals, for the case of press cure. As is evident from Comparative Example C3, high adhesive strength is not achieved by the presence of the component (C) alone (e.g. glycidylxypropyltrimethoxysilane) but
- 25 only in conjunction with component (B) according to the invention. As is evident from Comparative Example C4, furthermore, high adhesive strength is achieved not

by the presence of the component (B) alone but only in conjunction with a component (C) according to the invention. This is evidence of a synergistic effect of the adhesion-promoting components (B) and (C) of the silicone elastomer material according to the invention.

5     Vulcanization characteristics, optical and mechanical properties and compression set of addition-crosslinking silicone materials according to the invention and not according to the invention (Example 7 and Comparative Examples C5 and C6)

10           To assess the property profile of the self-adhesive silicone elastomer materials according to the invention and not according to the invention, 200.0 g of an addition-crosslinking liquid silicone elastomer material which is free of crosslinking agent, containing 71.6% by weight of diorganopolysiloxane having a viscosity of 20,000 mPa·s and 28.4% by weight of reinforcing filler, obtainable from Wacker-Chemie GmbH under the name ELASTOSIL® LR 3003/40 A, were thoroughly mixed with an amount, described in the following Examples C5, 7, and 15     C6, of adhesion-promoting additive which simultaneously serves as crosslinking agent, degassed under a vacuum of 10 mbar, filled into a compression mold and crosslinked at a temperature of 175°C for 10 min to give a 2 mm thick silicone elastomer film. The film was characterized with respect to transparency and mechanical properties (Shore A according to DIN 53505; elongation at break and 20     tensile strength according to DIN 53504; resilience according to DIN 53512; tear propagation strength according to ASTM D 624 B; compression set according to DIN 35517, 22 h / 175°C). Furthermore, the crosslinking characteristics of the freshly prepared uncrosslinked silicone material was determined by vulcametry (initiation temperature; crosslinking rate; maximum torque).

25     Comparative Example C5

2.1 g of the adhesion-promoting additive described in Comparative Example C1 are used according to the process described above. The results are shown in Tables 3 and 4.

### Example 7

2.6 g of the adhesion-promoting additive described in Example 1 are used according to the process described above. The results are shown in Tables 3 and 4.

### Comparative Example C6

- 5 0.18 g of phosphonitrilic chloride, prepared according to US-A-4,203,913, is added, at room temperature, with continuous stirring, to 250 g of a methylhydrogenpoly-siloxane,  $\text{Me}_3\text{Si}(-\text{O}-\text{SiH}(\text{Me}))_n-\text{O}-\text{SiMe}_3$ , which has terminal trimethylsilyloxy groups and, according to  $^{29}\text{Si}$ -NMR, has a number average chain length of  $n=53$ , and 750
- 10 g of a siloxane copolymer having terminal trimethylsilyloxy groups, consisting of dimethylsilyloxy and methylphenylsilyloxy units and having a viscosity of 100 mPa·s, measured at 25°C. After application of a vacuum of <20 mbar, stirring is carried out for 5 min and the vacuum is then broken with  $\text{N}_2$ . Stirring is then carried out for 2 h at a temperature of 100°C. 1.5 g of hexamethyldisilazane are added and stirring is carried out for a further 15 min. Finally, a vacuum of <10 mbar is applied, the
- 15 mixture is freed from volatile components with continuous stirring for 1 h at 100°C, the vacuum is broken with  $\text{N}_2$ , cooling to room temperature is effected, and the reaction product is filtered. 933 g of a clear silicone oil having a viscosity of 175 mPa·s and a content of 0.39% by weight of Si-bonded hydrogen are obtained. According to the  $^{29}\text{Si}$ -NMR spectrum, the reaction product is a siloxane copolymer
- 20 having terminal trimethylsilyloxy groups and consisting of  $-\text{O}-\text{Si}(\text{Me})_2-$ ,  $-\text{O}-\text{SiH}(\text{Me})-$  and  $-\text{O}-\text{Si}(\text{Me})\text{Ph}-$  units in a molar ratio of 25.9:36.2:37.9. The preparation of the adhesion-promoting additive which is used in an amount of 4.0 g according to the process described above is carried out by mixing 10 parts by weight of glycidyloxypropyltrimethoxysilane with 30 parts by weight of the reaction product
- 25 described above. The results are shown in Tables 3 and 4.



Table 3: Transparency and crosslinking characteristics

Example	Transparency	Initiation temperature	Crosslinking rate	Maximum torque
		[°C]	[Nm/min]	[Nm]
C5	translucent	105	1.09	0.46
7	translucent	114	0.52	0.36
C6	milky turbid	103	0.13	0.19

The results of the measurements shown in Table 3 demonstrate the disadvantages with regard to transparency and crosslinking characteristics of comparative self-adhesive silicone elastomer materials not according to the invention, whose SiH-containing component is distinguished by higher contents of incompatible radicals (> 12 mol%). In addition to increasing turbidity of the crosslinked silicone elastomer, there is also increasing inhibition of the crosslinking reaction, necessitating a limitation of the content of incompatible radicals of the component (B) to < 12 mol%, as in the silicone materials according to the invention.

Table 4: Mechanical properties

Example	Shore A	Elongation at break	Tensile strength	Resilience	Tear propagation strength	Compression set
		[%]	[N/mm <sup>2</sup> ]	[%]	[N/mm]	[%]
C5	39	650	8.6	54	25.0	44
7	34	750	8.7	49	23.8	48
C6	26	950	8.5	36	33.7	75

The values of the mechanical properties of the vulcanized products, shown in Table 4, demonstrate the considerable impairment of the crosslinking which occurs in the case of a very high content of incompatible radicals in the SiH crosslinking agent,

While embodiments of the invention have been illustrated and described,  
5 it is not intended that these embodiments illustrate and describe all possible forms of  
the invention. Rather, the words used in the specification are words of description  
rather than limitation, and it is understood that various changes may be made without  
departing from the spirit and scope of the invention.